

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

THERMAL AND DIELECTRIC PROPERTIES OF BLENDS OF POLYMETHYLMETHACRYLATE AND ATACTIC POLY-3-HYDROXYBUTYRATE

Giuseppina Ceccorulli^a; Mariastella Scandola^a

^a Department of Chemistry "G.Ciamician", Centro di Studio per la Fisica, University of Bologna, Bologna, Italy

Online publication date: 23 February 1999

To cite this Article Ceccorulli, Giuseppina and Scandola, Mariastella(1999) 'THERMAL AND DIELECTRIC PROPERTIES OF BLENDS OF POLYMETHYLMETHACRYLATE AND ATACTIC POLY-3-HYDROXYBUTYRATE', Journal of Macromolecular Science, Part A, 36: 2, 327 – 337

To link to this Article: DOI: 10.1081/MA-100101533

URL: <http://dx.doi.org/10.1081/MA-100101533>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NOTE

THERMAL AND DIELECTRIC PROPERTIES OF BLENDS OF POLYMETHYLMETHACRYLATE AND ATACTIC POLY-3-HYDROXYBUTYRATE

Giuseppina Ceccorulli and Mariastella Scandola*

University of Bologna

Department of Chemistry "G.Ciamician"

and Centro di Studio per la Fisica

delle Macromolecole del C.N.R.

via Selmi 2, 40126 Bologna, Italy

Key Words: Blend, Physical Properties, Polymethylmethacrylate, Poly-3-hydroxybutyrate

ABSTRACT

Polymethylmethacrylate (PMMA) was blended with variable amounts (from 9 to 46 wt%) of atactic poly-3-hydroxybutyrate (a-PHB) and films were compression molded. The blends were characterized by TGA, DSC and dielectric spectroscopy (DETA). The TG curves of a-PHB/PMMA blends show two TGA weight losses attributed to thermal degradation of a-PHB (the lower temperature one) and PMMA (at about 400°C). The DSC curves of the blends after melt quenching show a composition dependent glass transition which follows Wood's equation. Over the composition range, investigated a-PHB/PMMA blends are miscible. The DETA spectrum of the blends contains a sub- T_g relaxation associated with the secondary β relaxation of PMMA, whose temperature and apparent activation energy increase with increasing a-PHB content.

*Author to whom correspondence should be addressed.

INTRODUCTION

In an earlier paper, [1] the miscibility of polymethylmethacrylate (PMMA) with bacterial poly-3-hydroxybutyrate (PHB) was investigated. The interest in PHB/PMMA blends originated from the acquired acceptance of PMMA in biomedical applications and from the reported biocompatibility [2] of natural PHB. The blends showed a solubility limit of PHB in PMMA around 20 wt% PHB [1]. Contents of the natural polymer exceeding 20% were present in PHB/PMMA blends as a pure partially crystalline PHB phase.

In this work, we report the thermal and dielectric properties of blends of PMMA with atactic poly-3-hydroxybutyrate (a-PHB) synthesized via anionic polymerization [3]. Unlike the natural polyester, which very easily crystallizes due to its complete (100%) stereoregularity, the synthetic PHB used in this work, being atactic, is unable to develop a crystalline phase. Hence, in the present a-PHB/PMMA blends, both components are amorphous and the phase behavior is expected to be much simpler than when one of the components can crystallize and may phase separate even in miscible blends above the glass transition temperature.

EXPERIMENTAL

Atactic poly-3-hydroxybutyrate (a-PHB, $M_n=3000$, by vapor pressure measurements), synthesized as reported elsewhere [3], was kindly provided by Dr. M. Kowalczyk. Atactic polymethylmethacrylate (PMMA, $M_n=169000$, $M_w=350000$, by GPC) was a commercial product purchased from the Poly-science Company.

Blends of a-PHB with PMMA (a-PHB/PMMA) with different a-PHB content (5, 9, 15, 27, 36 and 46 wt%) were prepared by solution casting from chloroform followed by compression molding in a Carver laboratory press at 110°C for 2 minutes under a pressure of 0.5 tons/m². Pure PMMA was compression molded at 200°C for 3 minutes. All samples, obtained in the form of films, had a thickness of approximately 0.2 mm. Atactic PHB was a very sticky material from which no film could be obtained.

Thermogravimetric (TG) measurements were carried out with a Perkin Elmer TGA7 under nitrogen flow (20 ml/min), at a heating rate of 10°C/min.

Calorimetric (DSC) measurements were performed using a TA-DSC2010. The temperature scale was calibrated with high-purity standards. After prelim-



inary heating to 150°C (to remove the effects of previous thermal history) followed by quenching to -80°C, DSC scans were carried out over the temperature range from -80 to 150°C at a heating rate of 20°C/min. The glass transition temperature (T_g) was taken as the midpoint of the specific heat increment at the glass transition. The width of the glass transition on the temperature scale, ΔT_g , is taken as the temperature interval between the intercepts of the baselines below and above T_g and the tangent to the specific heat increment.

Dielectric measurements were carried out with a DETA instrument (Polymer Laboratories). In order to eliminate small amounts of water absorbed by the film samples during room storage, a preliminary heating run up to 120°C was carried out in the DETA under vacuum. Then, dry nitrogen was introduced in the measuring chamber, the temperature was lowered and measurements were performed at five selected frequencies (0.03, 0.1, 0.3, 1, 3 kHz) from -120°C to 120°C, at a heating rate of 1°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric (TG) curves of α -PHB/PMMA blends, and of plain α -PHB for the purpose of comparison. In agreement with earlier results on both natural [4] and synthetic [5] PHB, the polyester shows a single weight loss centered around 260°C.

The decomposition process of all α -PHB/PMMA blends occurs in two steps. The temperature of the first weight loss gradually increases with PMMA content in the blend. Its magnitude parallels the decrease of α -PHB content, suggesting that the first step in the TG curves of the blends originates from degradation of the α -PHB component. The second step is observed in all blends at about 400°C, the temperature range where the main thermal degradation of the PMMA used in this work is observed (data not shown). The entity of the second weight loss in Figure 1 is roughly proportional to PMMA content and is clearly associated with volatilization of the thermal degradation products of the PMMA component in α -PHB/PMMA blends.

The DSC determination of the glass transition temperature (T_g) is a simple and useful method to investigate miscibility of polymer blends. In a blend the presence of a single T_g intermediate to those of the pure components is usually taken as an indication of miscibility. All the DSC curves of the α -PHB/PMMA blends investigated show a single glass transition that shifts to lower temperature with increasing α -PHB content. The T_g of α -PHB/PMMA blends is



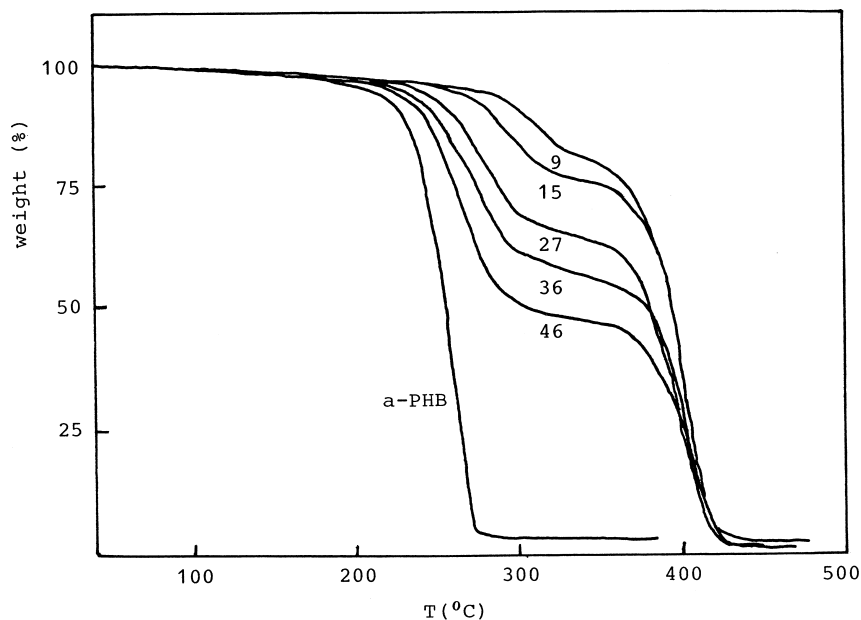


Figure 1. Thermogravimetric curves of a-PHB/PMMA blends with different composition. The number on curves is the a-PHB content (wt%).

plotted in Figure 2 as a function of composition. The regular change with a-PHB content indicates an extensive degree of compatibility of the blend components.

The curve drawn in Figure 2 represents Wood's equation [6]:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) \quad (1)$$

where T_g is the glass transition temperature of the blend, w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} are the T_g 's of a-PHB and PMMA, respectively, and k is an adjustable parameter ($k=0.22$ in the curve of Figure 2). Equation 1 is one of the well-known relationships used to describe the T_g -composition dependence in plasticized polymers and in miscible polymer blends. The very good fit to the experimental results observed in Figure 2 indicates miscibility of PMMA with a-PHB.

Each T_g in Figure 2 is associated with a vertical bar representing the width of the phenomenon. As expected, the glass transition of the blends is broader than that of the pure components, whose ΔT_g is of the order of a few degrees. Broadening of the glass transition is a common feature in both plasticized polymers and miscible polymer blends and is commonly attributed to the pres-



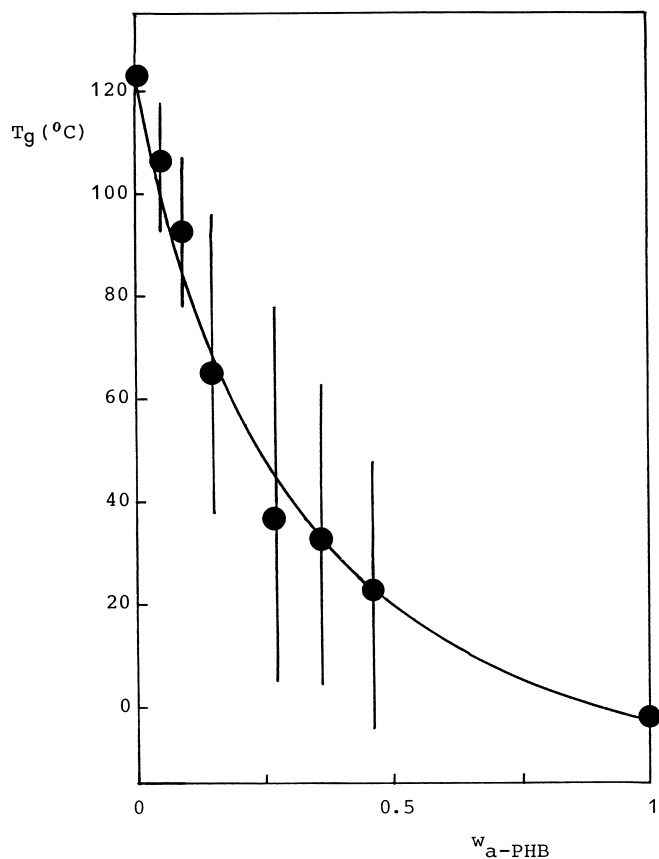


Figure 2. Glass transition temperature (T_g) of a-PHB/PMMA blends as a function of a-PHB weight fraction. The bar indicates the transition width (ΔT_g , see text).

ence of local composition fluctuations which give rise to a distribution of T_g values. In the blends investigated, this effect is particularly marked in the range of a-PHB contents 20-50%.

In order to further investigate the origin of the remarkable glass transition width in a-PHB/PMMA blends, Figure 3 compares the glass transition of the blend containing 46 wt% a-PHB with that of a copolymer with the same composition, obtained by grafting atactic PHB side chains onto the PMMA backbone as reported in a previous paper [7]. Also shown in Figure 3 are the T_g 's, as well as the transition start and end temperatures, whose difference represents the transition width, ΔT_g . It is observed that a-PHB/PMMA blend and the (MMA-g-HB) copolymer with the same composition have very close T_g but quite different

Downloaded At: 13:28 24 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

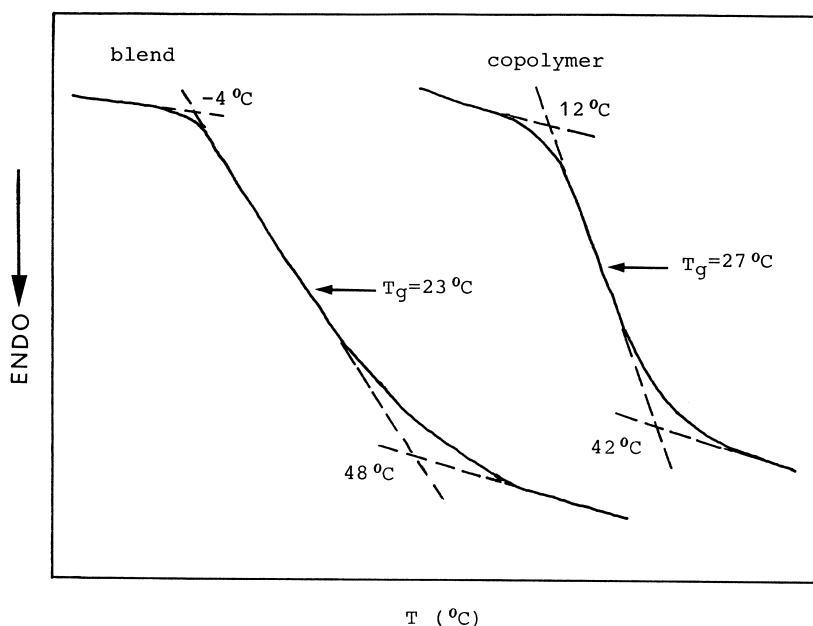


Figure 3. Comparison of the DSC curve of a-PHB/PMMA blend (46% a-PHB content) with that of a (MMA-g-HB) graft copolymer with the same composition. The DSC curves are shifted on the temperature scale for the sake of clarity.

glass transition width ΔT_g (52°C and 30°C for blend and copolymer, respectively). The glass transition of the copolymer is much sharper than that of the blend. It seems reasonable to suggest that the covalent bond, which chemically links the two polymeric species in the graft copolymer, forces the two components to a more close interaction than in the blends. Consequently, the copolymer has a narrower distribution of local concentration fluctuations and its glass transition is characterized by a smaller ΔT_g .

Figure 4 shows the dielectric spectrum at 30 Hz of PMMA and of its blends with different amounts of a-PHB. The measurements were preceded by careful sample drying (see Experimental) in order to eliminate absorbed water which has a pronounced effect on the relaxation spectrum [8]. In Figure 4, PMMA shows two relaxation regions denoted α and β in order of decreasing temperature. The higher temperature dielectric loss (α) is associated with the glass transition and compares favorably with the T_g of PMMA by DSC. The intense dielectric β relaxation of PMMA is commonly attributed [9] to motion of the side chain around the connecting bond to the backbone. The large dipole



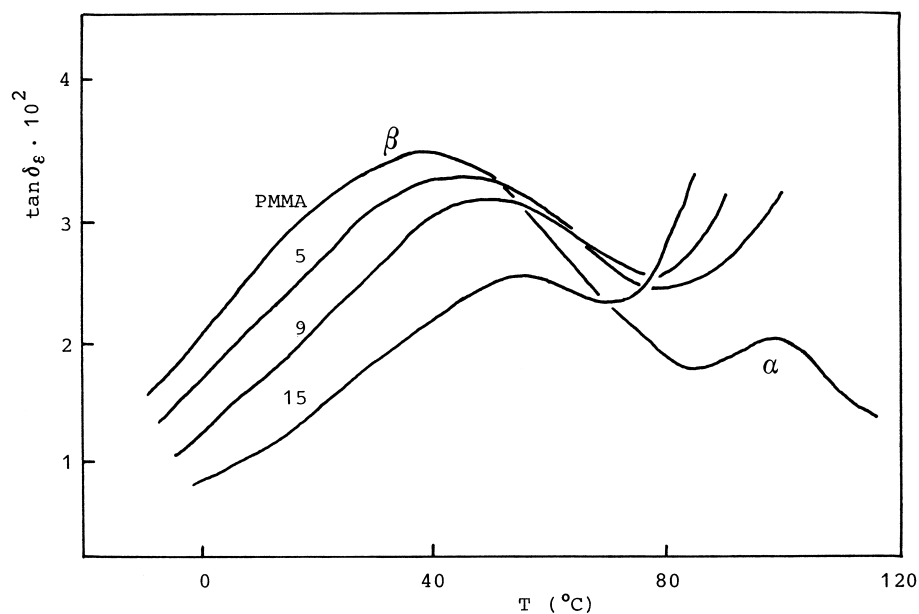


Figure 4. Dielectric spectrum of PMMA and of a-PHB/PMMA blends (frequency: 30Hz). The number on curves is the a-PHB content (wt%).

moment associated with the ester side group substantially contributes to the observed prominence of the β relaxation in the dielectric spectrum of PMMA.

The dielectric spectra of a-PHB/PMMA blends show on the high-temperature range a steep increase of $\tan \delta_\epsilon$. The temperature where the loss factor increases changes with blend composition (i.e. decreases with increasing a-PHB content) following the same trend as the DSC glass transition reported in Figure 2. The $\tan \delta_\epsilon$ increase in Figure 4 clearly indicates the onset of the large-scale motions typical of the glass-to-rubber transition but, as often observed in dielectric measurements, [10] the concomitant strong increase of d.c. conductivity prevents observation of the whole glass transition phenomenon in a-PHB/PMMA blends. The effect of d.c. conductivity becomes more and more important as a-PHB content in the blends increases. For this reason, no dielectric spectra could be collected for a-PHB/PMMA blends with a-PHB content higher than 15%.

In Figure 4, the blends show a low temperature relaxation whose intensity and temperature location change with a-PHB content. The peak temperature (T_{\max}) is reported in Table 1 together with that of the β relaxation of PMMA, for the sake of comparison. In order to get an insight into the nature of the dielectric



loss of a-PHB/PMMA blends, multi-frequency dielectric measurements were performed and the apparent activation energy ΔH_a of the process was evaluated from Arrhenius-type plots:

$$\nu = \nu_0 \exp(-\Delta H_a / RT_{\max}) \quad (2)$$

where ν is the measurement frequency. Figure 5 shows the relaxation data of the blends (and of plain PMMA for the sake of comparison), plotted according to the linear form of equation (2), i.e. as $\ln \nu$ vs. $1/T_{\max}$. In all cases, a good linear correlation is observed, from whose slope the apparent activation energy of the relaxation can be obtained. The ΔH_a values are reported in Table 1. The activation energy of the β relaxation of PMMA closely agrees with earlier literature results, [9] whereas the blends show ΔH_a values which increase with a-PHB content. An analogous behavior is observed for the relaxation peak

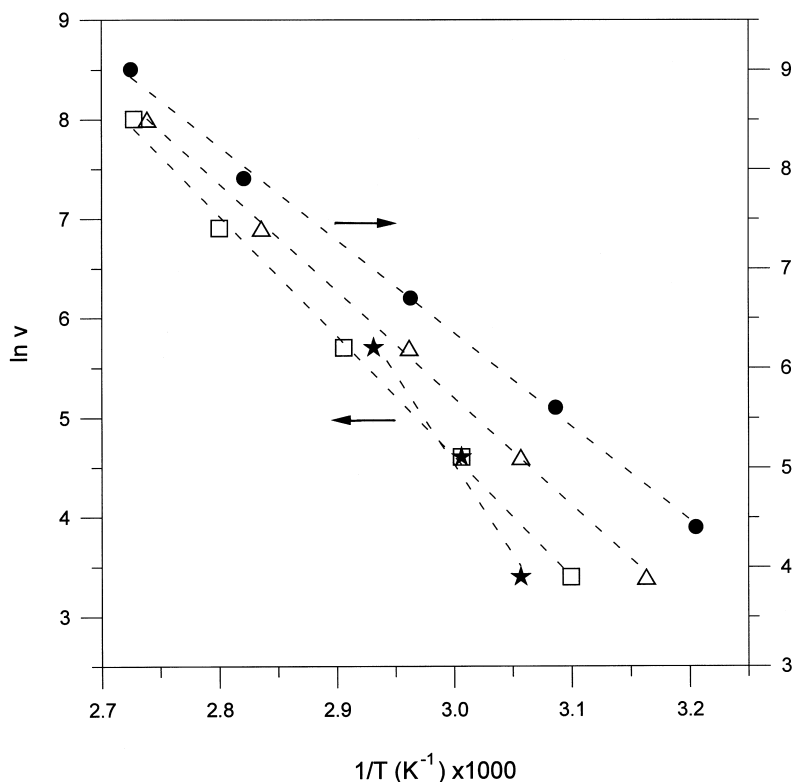


Figure 5. Arrhenius plot of the β relaxation of PMMA (●, frequency axis: right) and of the low-temperature dielectric relaxation of a-PHB/PMMA blends (frequency axis: left; a-PHB content in wt%: 5 (Δ), 9 (□) and 15 (★)).



TABLE 1. Parameters of the Dielectric Relaxation of a-PHB/PMMA Blends.

a-PHB (weight %)	T _{max} (°C, 30 Hz)	ΔH _a (KJ/mol)
0	39 ^{a)}	18 ^{a)}
5	43	21
9	49	24
15	54	36

a) dielectric β relaxation of PMMA

temperature (see T_{max} at 30 Hz in Table 1), that increases with the amount of a-PHB in the blend.

In this connection, it is known and quite easily understandable, that in local-mode secondary relaxations an increase of activation energy of the molecular motion responsible for the relaxation implies an increase of the temperature at which the relaxation occurs (at the same frequency). Some years ago, Heijboer [11] showed that activation energy and peak temperature follow a linear correlation, which is the same (at a fixed frequency) for a very large number of secondary local-mode relaxations (regarding both the main- and side-chains) in a broad range of different polymers. Based on such correlation, it is possible to predict the activation energy of a secondary glassy-state relaxation by simply knowing its temperature at a given reference frequency (usually 1 Hz). When the results of Table 1 are examined in the light of these considerations it is found that, while the parameters of PMMA β relaxation fit Heijboer's correlation, those of the blends' dielectric relaxation do not. In other words, in the blends, the activation energy increases with T_{max} more than expected on the basis of Heijboer's predictions for pure local-mode relaxations.

A possible explanation for the observed behavior is that in a-PHB/PMMA blends the nature of the molecular motion responsible for the low-temperature relaxation changes with composition from essentially local (as in plain PMMA) to partially cooperative, the latter type of motion obviously requiring a greater activation energy. In a-PHB/PMMA blends, it has been shown (see Figure 2) that a-PHB acts as a polymeric plasticizer by lowering T_g. As a consequence, with increasing a-PHB content the glass transition gets progressively closer to the dielectric relaxation region (Figure 4). It is suggested that the proximity of the glass transition, a process which involves cooperative motions of long chain



segments, induces a change of nature of the low-temperature relaxation of a-PHB/PMMA blends from essentially local to partially cooperative. Accordingly, with increasing a-PHB content both temperature and activation energy of the dielectric relaxation process of a-PHB/PMMA blends increase (see Table 1).

CONCLUSION

The blends of PMMA with atactic PHB have been found to be miscible. This result differs from that previously obtained using isotactic natural PHB [1] which showed limited miscibility with PMMA. The difference of miscibility behavior observed may be attributed to the large molecular weight difference of the polyester blended with PMMA in the two studies: a high molecular weight natural PHB in the previous investigation ($M_n = 350000$), and the present low molecular weight atactic PHB ($M_n = 3000$). The results of this work are in line with the common finding that blend miscibility increases when the molecular weight of the component polymers decreases.

REFERENCES

- [1] N. Lotti, M. Pizzoli, G. Ceccorulli, and M. Scandola, *Polymer*, **34**, 4935 (1993).
- [2] P. A. Holmes, in *Developments in Crystalline Polymers*, D. C. Bassett, Ed., Vol. 2, Elsevier, New York, 1988.
- [3] Z. Jedlinski, M. Kowalczyk, W. Glowkowski, and J. Grobelny, *Macromolecules*, **24**, 349 (1991).
- [4] N. Grassie, E. J. Murray, and P. A. Holmes, *Polymer Degrad. Stability*, **6**, 95 (1984).
- [5] M. Scandola, M. L. Focarete, M. Gazzano, A. Matuszowicz, W. Sikorska, G. Adamus, P. Kurcok, M. Kowalczyk, and Z. Jedlinski, *Macromolecules*, **30**, 7743 (1997).
- [6] L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).
- [7] M. Kowalczyk, G. Adamus, and Z. Jedlinski, *Macromolecules*, **27**, 572 (1994).
- [8] Manuscript in preparation.
- [9] N. G. McCrum, B. E. Read, and G. Williams, in *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.



- [10] R. H. Boyd, in *Electrical Methods in Methods of Experimental Physics*, Vol. 16, Part C, R. A. Fava, Ed., Academic Press, New York, 1980, pp. 379-421.
- [11] J. Heijboer, in *Molecular Basis of Transitions and Relaxations*, D. J. Meier, Ed., Gordon and Breach, New York, 1978.

Received July 20, 1998

Final revision received October 10, 1998



Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

[Order now!](#)

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081MA100101533>